

Selective oxidation of CO with modified Pd/ZnO catalysts in the presence of H₂: Effects of additives and preparation variables

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Abstract

Supported Pd catalysts on various support materials, ZnO, Ga₂O₃, SiO₂, CeO₂, In₂O₃, and Al₂O₃, exhibit poor activity and selectivity for the selective oxidation of CO in H₂-rich gas with O₂. The most active catalyst is Pd/ZnO among the six samples examined. The Pd species exist in the form of PdZn alloy in this catalyst and the alloy is more effective for the reaction compared with metallic Pd species of the other catalysts. The activity of Pd/ZnO catalyst can be significantly improved by the addition of alkali compounds, in particular Cs and Rb. These additives were shown to enhance the CO oxidation but suppress the undesired H₂ oxidation. With the optimized Cs-modified Pd/ZnO catalyst (Cs/Pd = 3), the CO concentration of a mixture of CO/O₂/H₂/CO₂ (0.5/2.0/23/7.0) can be reduced to a 40 ppm level at 433 K, while controlling the H₂ conversion level to <10%. Temperature programmed desorption measurements indicate that the addition of Cs affects the adsorption/desorption behavior of CO and H₂ on PdZn alloy particles in the Pd/ZnO catalyst but not the size of PdZn alloy crystallites. The Cs promoter is effective to weaken the strength of CO adsorption on the catalyst and increase the amount of H₂ weakly interacting with them in the presence of both CO and H₂, resulting in the enhanced selective CO oxidation activity of the Cs-modified Pd/ZnO catalyst.

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1. Introduction

Among various types of fuel cells, proton exchange membrane fuel cell (PEMFC) seems to be the most technically advanced system for transportation and stationary power units because of compact size, low operation temperature, high power density and rapid start up [1,2]. In this system, hydrogen is used as a fuel but it is not suitable for transportation due to its low boiling point. The hydrogen can be produced from natural gas, gasoline or alcohols (methanol and ethanol) by partial oxidation or steam reforming [3]. The reformat gases always contain CO and the Pt electrode of PEMFC is easily deteriorated by the adsorbed CO. Therefore, it is important that CO concentration must be kept at the level to a tolerable range below 50 ppm [4]. CO can be partially converted to CO₂

via the water gas shift reaction (WGSR), but the concentration of CO is thermodynamically limited to levels of about 0.5–1% [5]. Hence, further effective CO removal process is required. The selective oxidation of CO has been regarded to be one of the most promising methods to reduce the CO concentration down to ppm level in the H₂-rich reformat gases [6].

The catalysts that have so far been reported for the selective oxidation of CO are alumina supported platinum-group metals (Pt, Ru and Rh) [2,5,7–10], zeolite supported Pt catalysts [11–13] and gold-based catalysts [14,15]. The gold-based catalysts are more active than platinum-group metal catalysts at lower temperatures below 400 K, but deactivation occurs in the presence of CO₂ in the feed stream [16]. Pd-based catalysts are less active for the selective oxidation of CO in the presence of H₂ [7,13,17]. The performance of supported metal catalysts may be changed by adding some promoter or modifier [2,18–29]. When alkali metals, such as Na or K, are added to Pt or Rh-based catalysts, their catalytic performance is significantly improved [18–22]. Tanaka et al. found a highly active and

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selective new catalyst, which was prepared by loading a large amount of Fe-oxide on 1 wt% Pt supported on TiO₂, Al₂O₃ and CeO₂ [27,28]. More recently, Mirkelamoglu and Karakas [26] have reported that alkali metal enhances CO oxidation activity of PdO/SnO₂ catalysts. In this work, however, experiments were run with only CO and O₂ in the absence of H₂.

Recently, we have communicated that Pd/ZnO catalysts are active for the selective CO oxidation in H₂-rich than several supported Pd catalysts using different supports and, in addition, the activity of Pd/ZnO catalysts can be significantly improved by the addition of such alkali metals as Ca and Rb [30]. The present work has been undertaken to optimize preparation parameters for the design of more active Cs-promoted Pd/ZnO catalysts and examine their activity under different reaction conditions. Further, the adsorption/desorption behavior of CO and H₂ has been investigated using TPD methods to consider reasons for the enhanced CO oxidation activity of those catalysts.

2. Experimental

2.1. Catalyst preparation

Various supported Pd catalysts, such as Pd/Ga₂O₃, Pd/SiO₂, Pd/CeO₂, Pd/In₂O₃, and Pd/Al₂O₃ were prepared by impregnation methods similar to those used previously [31]. CeO₂ was obtained by thermal decomposition of Ce₂(CO₃)₃·nH₂O at 773 K and the others were purchased and used without further purification, Ga₂O₃ (Kishida Chemical, 99.99%), SiO₂ (GL Sciences, 99.0%), In₂O₃ (Wako Pure Chemical, 99.9%) and Al₂O₃ (Nishio Industry, 99.7%). The support material was impregnated with a solution of palladium nitrate at 353 K. Pd/ZnO catalyst was prepared by a precipitation method [32], in which an aqueous solution of sodium carbonate was added to a mixed solution of palladium and zinc nitrates until pH 8 at 353 K under continuous stirring. The precipitate formed was then filtered out, washed with cold and hot distilled water, and dried in air at 383 K. The residual amount of sodium remaining in the Pd/ZnO samples obtained was examined by X-ray fluorescence and it was found to be below the detectable limit. Alkali metal modified Pd/ZnO catalysts were prepared by impregnation of a Pd/ZnO sample with a solution of alkali metal carbonate, such as Li₂CO₃, Na₂CO₃, K₂CO₃, Rb₂CO₃ or Cs₂CO₃. For Cs-modified Pd/ZnO catalysts, CsNO₃ and CsOH were also used as a source of Cs. The Pd loading was 1 wt% unless otherwise stated. The catalyst samples thus prepared were calcined in air at 773 K for 3 h, followed by reduction before reaction runs, as described below.

2.2. Activity measurement

The preferential oxidation of CO was carried out with a glass fixed bed flow-type reactor in a temperature range of 353–473 K. A weighed sample of catalyst (0.1 g) was pretreated in the reactor under a stream of O₂ (20 vol.% O₂) diluted with N₂ at 773 K for 2 h and then cooled to room temperature. The sample was then reduced in a H₂ stream (4 vol.% in N₂) at room

temperature at 1 h and at increasing temperatures at 5 K min^{−1} up to 773 K. After the reduction, pure N₂ stream was introduced and the sample was cooled to reaction temperature. The reaction was started by introducing a mixture of CO/O₂/H₂/CO₂/N₂. The composition of inlet gases was 1.6% CO, 1.6% O₂, 7.0% CO₂ and 23.0% H₂ in N₂ as a diluents. In some cases, the concentration of CO and O₂ was changed from 0.3% to 1.6% and from 0.5% to 2.0%, respectively. The effluent gases were analyzed by gas chromatographs equipped with TCD and FID. For quantitative analysis for trace amount of CO, it was converted to methane by a Ni catalyst before supplying to FID.

The CO or H₂ conversion was calculated from the concentration of CO or H₂ at inlet and outlet: Conversion of X = ([X]_{in} − [X]_{out})/[X]_{in} (X = CO, H₂). Under the conditions used, only CO₂ and H₂O were observed to form without any other products. The O₂ conversion was calculated from the concentration of O₂ at inlet and those of CO and H₂: $\{([CO]_{in} - [CO]_{out})/2 + ([H_2]_{in} - [H_2]_{out})/2\}/[O_2]_{in}$. This was because the quantitative analysis of O₂ at outlet was not good in our GC measurements when it was small at large O₂ conversion. Selectivity for the CO oxidation was defined as the ratio of O₂ used for the oxidation of CO to the total amount of O₂ consumed by the oxidation of CO and H₂:

$$\text{Selectivity} = \{([CO]_{in} - [CO]_{out})/2\} / \{([CO]_{in} - [CO]_{out})/2 + ([H_2]_{in} - [H_2]_{out})/2\}.$$

2.3. Catalyst characterization

The catalysts prepared were characterized by X-ray diffraction (JEOL JDX-8020) using Cu Kα radiation (λ = 0.15405 nm) to examine their structural features. Temperature programmed reduction (TPR) was used to examine the reduction behavior of Pd precursors (mostly in the form of PdO) dispersed on different supports in the above-mentioned manners. A catalyst sample (1.0 g) was calcined in a 20% O₂ (in N₂) stream at 100 cm³ min^{−1} and at 773 K for 2 h and cooled down to room temperature. Then, the sample was reduced by 4% H₂ (in N₂) stream at room and increasing temperatures at 5 K min^{−1}. The amount of H₂ consumed was measured by TCD. The adsorption and desorption behavior of CO and H₂ over the surface of catalysts was examined with temperature programmed desorption (TPD) using a TPD apparatus (Nippon BEL TPD-A1) equipped with a TCD and a mass spectrometer. A catalyst sample (1.0 g) was calcined and reduced with the same procedures and finally reduced at 773 K for 90 min. Then, CO, H₂, or CO + H₂ was adsorbed on the catalyst sample; for CO, 5% CO (in He) was passed at room temperature for 60 min and, after flushing with pure He, the catalyst sample was heated at 5 K min^{−1} up to 873 K in a He stream at 50 cm³ min^{−1}. For H₂, a higher temperature of 373 K was used to avoid the formation of metal hydrides. The sample was exposed to a 4% H₂ (in N₂) stream at 100 cm³ min^{−1} and at 373 K for 60 min and cooled to room temperature in a pure N₂ stream. The catalyst temperature was raised at 5 K min^{−1} up to 1073 K in a N₂ flow at 500 cm³ min^{−1}. For co-adsorption of CO

and H₂, a mixture of 5% CO and 20% H₂ was passed over the catalyst at room temperature for 60 min, followed by TPD at 5 K min^{−1} up to 873 K.

3. Results and discussion

3.1. Activity of various supported Pd catalysts

The Pd catalysts using different support materials were compared for selective oxidation of CO in H₂-rich gas at 433 K. It was observed that oxidation of both CO and H₂ occurred and the conversion of either CO or H₂ slightly changed during an initial period of reaction. For all the catalysts examined, the conversion was observed to become to a steady-state level within 60 min. In the following, the results collected after a time on stream of 60 min are used to evaluate and compare the performance of the catalysts prepared.

Table 1 gives the activity of various supported Pd (1 wt%) catalysts, which show significant differences in the catalytic performance. The catalysts except for Pd/SiO₂ and Pd/Ga₂O₃ give higher O₂ conversion but smaller CO conversion levels <20%. The O₂ conversion of Pd/SiO₂ catalyst is lower compared with the other Pd catalysts. No reaction occurred over Pd/Ga₂O₃ catalyst. The highest CO conversion is obtained with Pd/ZnO catalyst, but its value is only 18%. Those results indicate that most of O₂ is consumed by the oxidation of H₂, giving poor selectivity for the CO oxidation over those supported Pd catalysts used; that is, the undesired oxidation of H₂ occurs in preference to the oxidation of CO.

The structural features of the catalysts were examined by XRD. Fig. 1 shows XRD patterns after the reactions at 433 K. A clear diffraction peak due to metallic Pd is seen with Pd/SiO₂ only. Such a diffraction peak is not observed with Pd/Al₂O₃, Pd/CeO₂, and Pd/Ga₂O₃, for which the amount of Pd supported is small and probably it is highly dispersed over the supports. The previous XRD results on the catalysts containing a larger amount of Pd (10 wt%) [31] suggest that the Pd species on Al₂O₃ and CeO₂ are metallic and those on Ga₂O₃ are Ga₅Pd and Ga₂Pd₅ alloys for the present catalysts with a smaller Pd loading of 1 wt%. For Pd/ZnO only a diffraction peak due to PdZn alloy is seen although it is weak. Stronger XRD peaks indicative of the PdZn alloy formation were observed for the

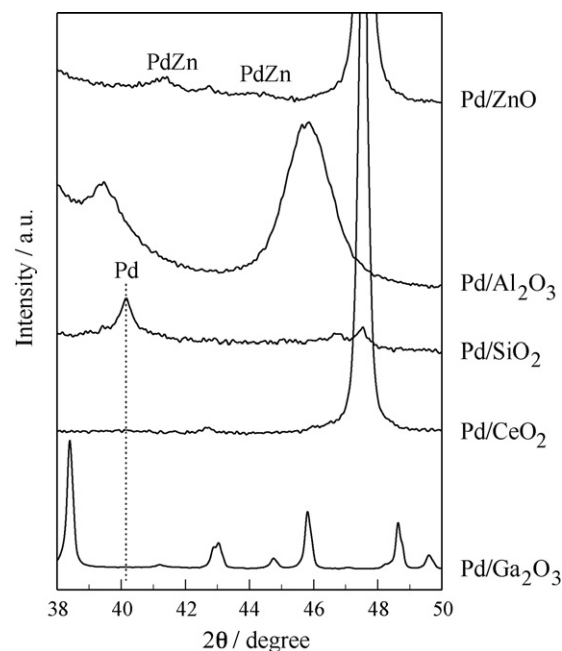


Fig. 1. XRD patterns for various supported Pd catalysts measured after reaction at 433 K for 2 h. Pd loading: 1.0 wt%.

Pd/Zn samples with larger Pd loadings [32]. It is assumed, therefore, that the PdZn alloy species are more effective for the selective CO oxidation in the H₂-rich gas compared with the other Pd species. The highest CO conversion of 18% is achieved with the Pd/ZnO catalyst, as above mentioned, but this conversion level is unsatisfactory. Then, attempts have been made to improve the catalytic activity of Pd/ZnO by using different preparation variables and reaction conditions and by modifying with alkali additives.

3.2. Activity of Pd/ZnO catalysts under different conditions

Fig. 2 shows results obtained over Pd/ZnO catalysts with different Pd loadings in a range from 0.1 to 10 wt%. The CO conversion increases marginally with Pd loading up to 0.5 wt%, above which it decreases markedly. The O₂ and H₂ conversion levels do not depend on the Pd loading so much, which are >70% and <10%, respectively. A maximum activity for the

Table 1
Comparison of the catalytic activity of various supported Pd catalysts at 433 K

Catalyst ^a	Surface area ^b (m ² g ^{−1})	Conversion (%)			Selectivity (%)
		CO	O ₂	H ₂	
Pd/ZnO	29	18	79	9.8	11
Pd/Ga ₂ O ₃	6	0	0	0	–
Pd/SiO ₂	620	5.2	16	1.9	16
Pd/CeO ₂	45	1.1	58	8.0	0.9
Pd/In ₂ O ₃	4	4.9	57	7.6	4.3
Pd/Al ₂ O ₃	148	12	59	7.4	10

Reaction conditions: CO 1.6%, O₂ 1.6%, H₂ 23%, CO₂ 7.0%.

^a Pd loading: 1.0 wt%.

^b BET surface area of supports, except for Pd/ZnO prepared by co-precipitation; the surface area of Pd/ZnO is given. The samples were pretreated under dynamic evacuation at 423 K for 2 h before BET measurements.

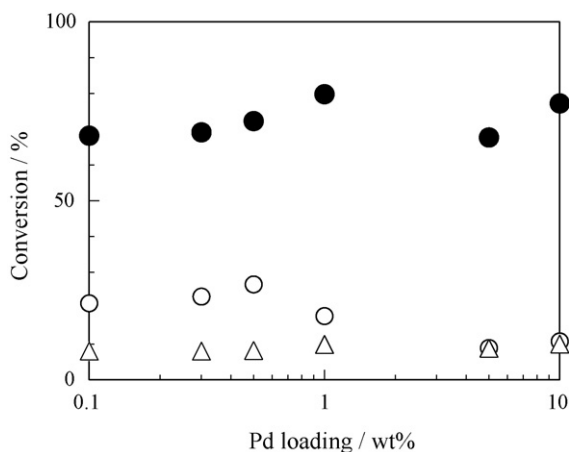


Fig. 2. Influence of Pd loading on the activity of Pd/ZnO catalyst at 433 K. (●) O₂, (○) CO and (△) H₂.

selective oxidation of CO may be obtained with a small Pd loading of 0.5 wt%. The BET surface area of 0.5, 1, and 5 wt% Pd/ZnO samples was 26, 29, and 36 m² g⁻¹, respectively, and so it is less significant for determining the catalytic activity.

The influence of reduction temperature was examined for a 0.5 wt% Pd/ZnO sample. The activities of the catalysts reduced at 473 and 773 K are compared in Fig. 3. With increasing reduction temperature from 473 to 773 K the CO conversion increases from 17% to 27% while the H₂ conversion marginally decreases. The total conversion of O₂ is high in either case. Fig. 4 gives XRD patterns of these two catalysts, indicating the presence of PdZn alloy in the catalyst reduced 773 K and no appreciable diffraction peaks for Pd species in the one reduced at 473 K. Using a Pd/ZnO sample with a larger Pd loading of 10 wt% the present authors previously showed that some fraction of Pd species were alloyed with Zn and metallic Pd and PdZn alloy coexisted after the reduction at a lower temperature of 473 K while almost all Pd species existed in the form of PdZn alloy at a higher reduction temperature of 773 K [33,34]. It is again indicated that the PdZn alloy is more effective for the selective oxidation of CO in H₂-rich gas.

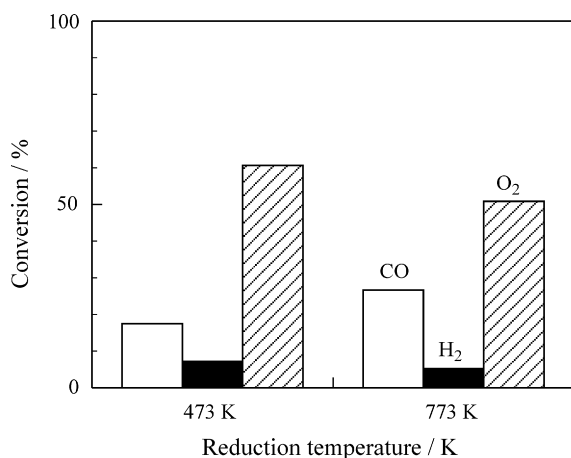


Fig. 3. Influence of reduction temperature on the activity of 0.5 wt% Pd/ZnO catalyst at 433 K.

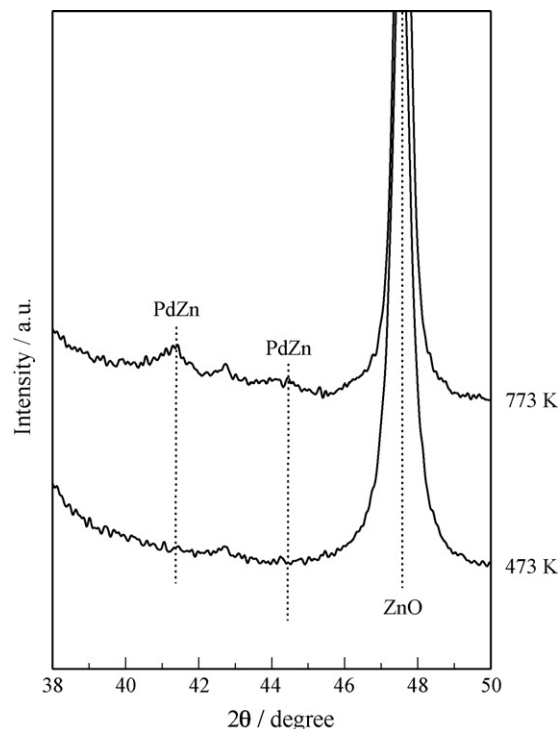


Fig. 4. XRD patterns for the 0.5 wt% Pd/ZnO catalysts reduced at 473 and 773 K.

The influence of reaction temperature was examined for the most active Pd/ZnO catalyst with a Pd loading of 0.5 wt% (Fig. 5). The reaction is very slow at 353 K but a CO conversion of 27% is obtained at 393 K, which slightly decreases with the reaction temperature. The O₂ conversion increases significantly at 393 K and then gradually at higher temperatures. Thus, as the reaction temperature is raised, the CO oxidation is suppressed while the H₂ oxidation is slightly enhanced for the present catalyst and conditions.

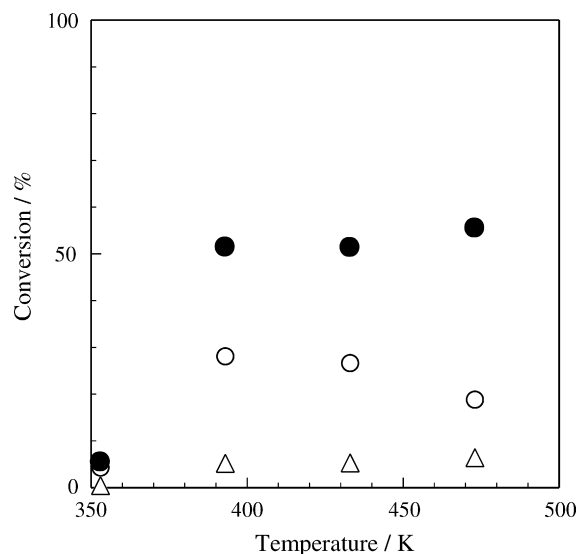


Fig. 5. Influence of reaction temperature on the activity of 0.5 wt% Pd/ZnO catalyst reduced at 773 K. (●) O₂, (○) CO and (△) H₂.

Table 2
Influence of H₂ concentration on the activity of 1 wt% Pd/ZnO catalyst at 433 K

H ₂ concentration (%)	Conversion (%)			Selectivity (%)
	CO	H ₂	O ₂	
0	7.1	–	3.6	100
1.55	67	99.8	82	41
23	18	9.8	79	11

Reaction conditions: CO 1.6%, O₂ 1.6%, CO₂ 7.0%.

The reaction was also conducted at different H₂ concentrations for a 1 wt% Pd/ZnO catalyst reduced at 773 K (Table 2). The CO conversion is low (7.1%) in the absence of H₂. It increases to 67% at 1.55% H₂ but it drops to 18% at a higher H₂ concentration of 23%. The O₂ conversion is high >80% in the presence of H₂. Recently, similar results were also reported by Tanaka and co-workers [29,35]. They found that the activity of FeOx/Pt/TiO₂ and FeOx/Au/TiO₂ catalysts for the CO oxidation is enhanced by the presence of H₂ due to a new reaction path via hydroxyl carbonyl intermediate. Table 2 indicates that a certain concentration of H₂ is needed for the Pd/ZnO catalyst to be active for the oxidation of CO. It was shown from temperature programmed oxidation that about 10% of Pd species in the 1 wt% Pd/ZnO sample was oxidized at temperatures up to a reaction temperature of 433 K [32]. It is thus likely that a larger surface area of PdZn alloy particles is oxidized and becomes less active during the reaction in the absence of H₂. In the presence of H₂, however, the surface of oxidized PdZn alloy particles may be reduced and remains catalytically active during the reaction. An excess amount of H₂ (23% against 1.6% CO) hinders the oxidation of CO.

3.3. Influence of additives in various supported Pd catalysts

As described above, the CO conversion can be improved to 27% with a 0.5 wt% Pd/ZnO catalyst reduced at 773 K. Further improvement was made by using additives of alkali compounds. Kunimori et al. have recently found that the activity of Rh/SiO₂ catalysts is improved upon the addition of potassium. The catalytic activities of Pd/ZnO samples modified with such alkali metals as K, Na, Li, Rb, and Cs were compared [30]. Those, except for Li, are effective for enhancing the catalytic activity for the selective CO oxidation, among which Cs and Rb are promising promoters. The Cs-modified Pd/ZnO shows a high CO conversion of 82% with a selectivity of 60%. It was also indicated that the O₂ conversion did not change so much on the addition of alkali compounds. Thus, these additives can suppress the oxidation of H₂ but significantly enhance the oxidation of CO.

3.4. Influence of Cs promoter on Pd/ZnO catalysts

For Cs-modified Pd/ZnO catalyst having the highest CO oxidation activity, the effects of Cs source and loading were further examined. Different Cs salts, such as carbonate (Cs₂CO₃), nitrate (CsNO₃) and hydroxide (CsOH), were used to prepare three Cs-modified catalysts (Cs/Pd = 3). These catalysts were

found to be very similar in the performance (CO and O₂ conversion). Cesium carbonate was used for further experiments.

Previously, the influence of Cs loading in the Cs-modified Pd/ZnO catalysts was examined, in which the quantity of Cs loaded was changed while keeping the Pd loading at 1 wt% [30]. The CO conversion drastically increases by the addition of a small amount of Cs with a Cs/Pd ratio of 0.5. A larger CO conversion is obtained with a ratio of 1. With further increasing Cs/Pd ratio up to 10, the CO conversion gradually decreases. The change of the selectivity with the Cs/Pd ratio is similar to that of the CO conversion. The O₂ conversion is high >65% at any Cs/Pd ratio examined. When a Cs/ZnO catalyst, in which no Pd was loaded, was used, no reaction was observed to occur under the reaction conditions used. Thus, the enhancement effect of Cs manifests itself in the presence of both Cs and Pd on ZnO support.

The catalytic features of Pd/ZnO and Cs-modified Pd/ZnO samples with a Cs/Pd ratio of 1 were compared by reactions with a stream of CO (1.6%) and O₂ (1.6%) in the absence of H₂ at 433 K. As shown in Section 3.2, the unmodified Pd/ZnO catalyst exhibits poor activity for the oxidation of CO, giving a small CO conversion of only 7.1%. For the latter, in contrast, CO was observed to be completely oxidized to CO₂. In addition, those two catalysts were subjected to reactions with a stream of H₂ (1.6%) and O₂ (1.6%) in the absence of CO. It has been shown that the H₂ conversion of Pd/ZnO catalyst is 100%, whereas that of Cs-modified Pd/ZnO catalysts is 70%. Those results demonstrate that the addition of Cs to Pd/ZnO catalyst significantly enhances its activity for CO oxidation but suppresses that for H₂ oxidation.

3.5. Activity of Cs-promoted Pd/ZnO catalysts under different conditions

The influence of reaction temperature was examined with the Cs-modified Pd/ZnO catalyst with a Cs/Pd ratio of 3. Fig. 6

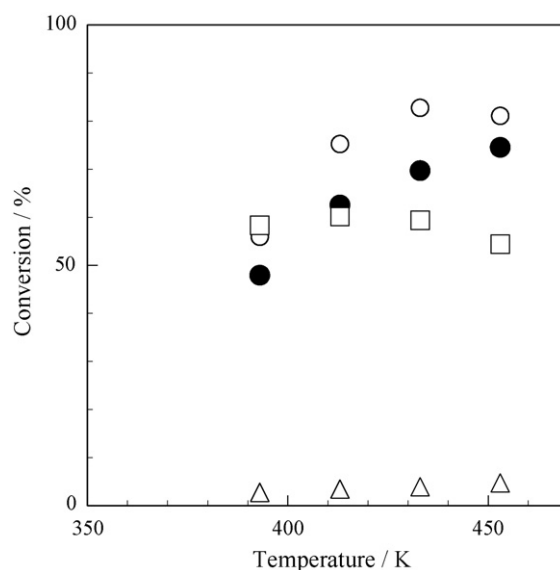


Fig. 6. Influence of reaction temperature on the activity of Cs-modified 1 wt% Pd/ZnO catalyst with a Cs/Pd ratio of 3. Conversion of (●) O₂, (○) CO, (△) H₂, and (□) Selectivity.

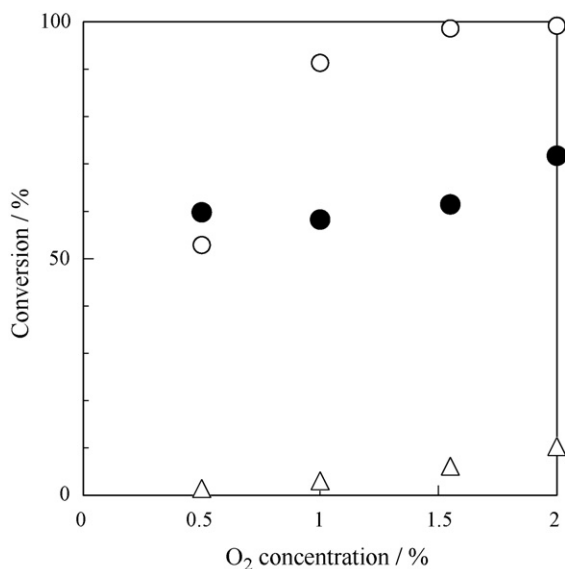


Fig. 7. Influence of O₂ concentration on the activity of Cs-modified 1 wt% Pd/ZnO (Cs/Pd = 3) catalyst at 433 K. The reactions were carried out at a constant CO concentration of 0.5%. (●) O₂, (○) CO and (△) H₂.

shows that the CO conversion increases with the temperature up to 433 K above, which it does not change at a temperature 453 K. The H₂ conversion slightly increases with the temperature but it is low even at 453 K. The O₂ conversion

also increases with the temperature, attaining 75% at 453 K. The selectivity for CO oxidation is almost constant at reaction temperatures examined.

Fig. 7 indicates the influence of O₂ concentration, in which the reactions were carried out at a constant CO concentration of 0.5%. The CO conversion increases with the O₂ concentration and it is almost completely oxidized at 1.6% or above. The concentration of the residual CO in the effluent obtained at an O₂ concentration of 2% is such a low level as 40 ppm, which is comparable to the level attainable with Pt-based catalysts [5]. Similar changes of CO and H₂ conversion with O₂ concentration were also observed at a higher CO concentration of 1.6%. The CO conversion obtained at 1.6% CO concentration is smaller than that at 0.5% when compared at the same O₂ concentration but it can also become to a high level >95% at an O₂ concentration of 2.5%.

3.6. Characterization and features of Cs-promoted Pd/ZnO catalysts

The structure of Cs-modified Pd/ZnO catalysts with different Cs/Pd ratios was examined by XRD (Fig. 8). All the catalysts examined have diffraction peaks ascribable to PdZn alloy. Previously, we found that when Pd/ZnO catalysts were reduced by H₂ at 773 K, the support was partially reduced and the resulting Zn was alloyed with supported Pd species

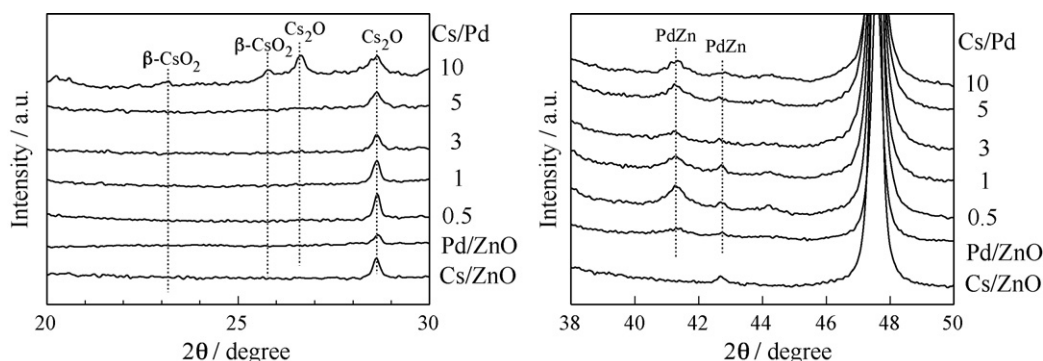


Fig. 8. XRD patterns for Cs-modified 1 wt% Pd/ZnO catalysts with different Cs/Pd ratios after reaction at 433 K for 2 h.

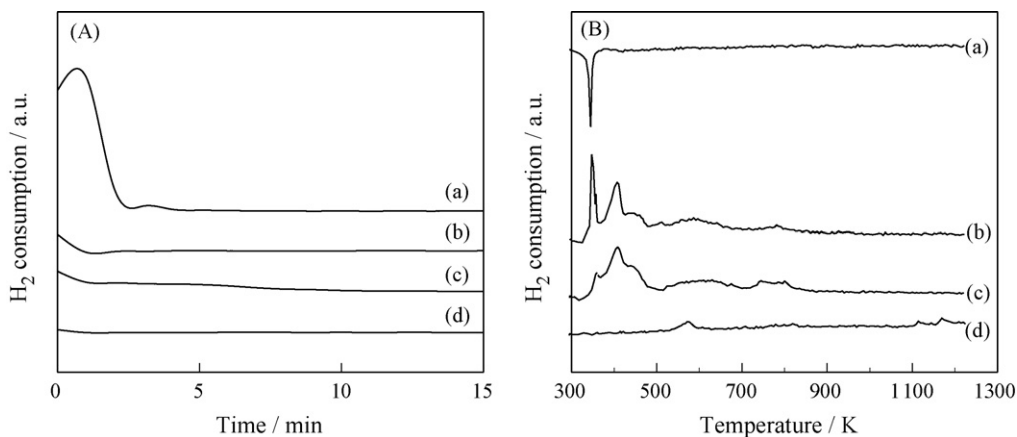


Fig. 9. TPR profiles for four different catalysts (A) at room temperature and (B) increasing temperatures. (a) 1 wt% Pd/SiO₂, (b) Cs-modified 1 wt% Pd/ZnO (Cs/Pd = 3), (c) 1 wt% Pd/ZnO and (d) 3.7 wt% Cs/ZnO catalysts.

Table 3

Amounts of H₂ consumed for TPR^a at room and at increasing temperatures

Catalyst	Pd loaded (mmol)	H ₂ consumed (mmol)		
		Room temperature	Increasing temperatures	Total
Pd/SiO ₂	0.093	0.12	−0.02 ^d	0.10
Cs/ZnO	(000) ^c	0.003	0.01	0.013
Pd/ZnO	0.093	0.04	0.20	0.24
Cs-Pd/ZnO ^b	0.091	0.03	0.21	0.24

^a TPR profiles are given in Fig. 11.^b Pd loading: 1.0 wt%; Cs/Pd = 3.^c Cs loading: 3.7 wt%.^d H₂ desorbed during TPR.

[32]. For the present catalysts, a higher reduction temperature of 773 K was used and the PdZn alloy particles were formed. Fig. 9 shows TPR profiles for four different catalysts at room temperature and increasing temperatures. For a reference sample of Pd/SiO₂, reduction of Pd precursors (PdO) occurred easily at room temperature at an excess amount of H₂ consumed than that for the complete reduction (Table 3) and a certain amount of H₂, which should be adsorbed and/or absorbed (hydrides), was desorbing at around 340 K. For another control of Cs/ZnO, the consumption of H₂ was very small. Fig. 9 and Table 3 indicate that for Pd/ZnO and Cs-modified Pd/ZnO samples, some fraction of Pd precursors was reduced at room temperature and the residual fraction at increasing temperatures. The addition of Cs is unlikely to affect the reduction behavior of Pd precursors on ZnO and the formation of PdZn alloys. The latter is suggested by similar TPR profiles and larger amounts of H₂ consumed than needed for the complete reduction of PdO present for these two samples. Other factors should be considered to explain the significant difference observed in the activity for the selective CO oxidation.

Kunimori et al. has reported that activity of Rh/SiO₂ catalyst for the selective oxidation of CO in H₂-rich gas is promoted by potassium. The size of Rh metal particles is reduced by the addition of potassium, resulting in an increase in the CO oxidation activity [20]. It has recently reported that for our supported Pd catalysts, the crystallite size of PdZn alloys in Cs modified Pd/ZnO with a Cs/Pd of 0.5 is the same as measured in the original Cs-free Pd/ZnO catalyst, in contrast to a fact that the activity of CO oxidation markedly increases by the addition of Cs [30]. In addition, the size of PdZn alloy crystallites increases with increasing Cs/Pd ratio, whereas the activity of CO oxidation goes through a maximum at a Cs/Pd ratio of 1. Thus, the enhanced activity of Cs-modified Pd/ZnO catalysts for the CO oxidation is not ascribable to reduction of the crystallite size of PdZn alloys. Kunimori et al. also reported that K₂CO₃-promoted Rh/USY catalyst exhibits much higher performance for the selective oxidation of CO than unpromoted Rh/USY catalyst [19]. They suggest that the electron transfer occurs from potassium to Rh, and this modifies CO adsorption strength of the Rh species. Such an electronic effect could also operate for our Cs-modified Pd/ZnO catalysts, which influences the adsorption of the reacting species of H₂, CO, and/or O₂ on the surface of these catalysts. The adsorption of these gases on our Pd catalysts was examined by TPD.

The features of selected supported Pd catalysts for adsorption/desorption of CO were examined by TPD of CO adsorbed at room temperature. Fig. 10 gives TPD profiles and Table 4 lists the amount of CO desorbing at temperatures up to 773 K. It is seen that CO little desorbs from Cs/ZnO and a certain amount of CO desorbs from Pd/SiO₂ in a wide range of temperature. Compared with Pd/SiO₂, smaller amount of CO desorbs from Pd/ZnO but almost all CO species desorbs at lower temperatures up to 530 K with a desorption maximum at about 373 K. A similar TPD profile is seen for Cs-modified Pd/ZnO and the Cs additive can increase the amount of CO desorbing at these low temperatures. The total quantities of CO desorbing are comparable between Cs-modified Pd/ZnO and Pd/SiO₂ catalysts, which are significantly different in the activity for the selective oxidation of CO, as described above. Thus, lower temperatures for CO desorption with the Cs-modified Pd/ZnO catalyst are important for its higher activity for the reaction.

TPD was also used to examine the features of the catalysts for the adsorption/desorption of H₂, which was adsorbed at 373 K to avoid the formation of palladium hydrides. The TPD profiles are presented in Fig. 11 and the total amounts of H₂ desorbing at temperatures examined are also listed in Table 4. It is seen that a certain quantity of H₂ desorbs from Pd-free Cs/ZnO at low temperatures <473 K. A larger quantity of H₂

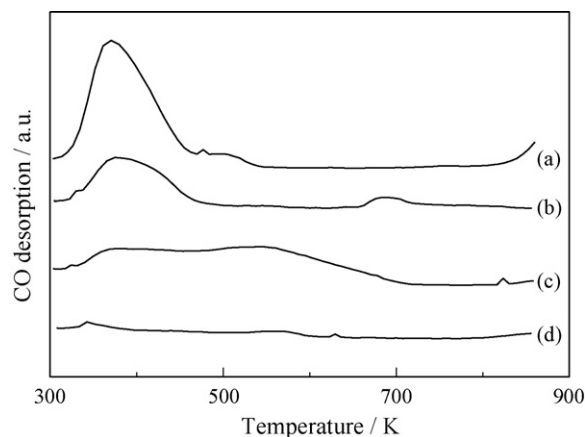


Fig. 10. CO-TPD profiles for four different catalysts. The catalysts were pretreated by 5 vol.% CO at room temperature for 1 h. (a) Cs-modified 1 wt% Pd/ZnO (Cs/Pd = 3), (b) 1 wt% Pd/ZnO, (c) 1 wt% Pd/SiO₂ and (d) 3.7 wt% Cs/ZnO catalysts.

Table 4

The amounts of CO and H₂ desorbing on TPD of CO, H₂, and CO + H₂

Catalyst ^a	CO (cm ³ g ⁻¹)		H ₂ (cm ³ g ⁻¹)	
	CO ^b	CO + H ₂ ^c	H ₂ ^d	CO + H ₂ ^c
Cs-Pd/ZnO	1.6×10^{-8}	0.7×10^{-8}	0.33	0.27
Pd/ZnO	1.0×10^{-8}	1.3×10^{-8}	0.29	0.24
Pd/SiO ₂	1.4×10^{-8}	1.8×10^{-8}	0.10	0.23
Cs/ZnO	0.07×10^{-8}	– ^e	0.07	0.06 ^f

^a Pd loading: 1.0 wt%.^b The catalysts were pretreated by 5 vol.% CO at room temperature for 1 h. CO desorbed in a temperature range from 300 to 700 K during the TPD.^c The catalysts were pretreated by a mixture of 5 vol.% CO and 20 vol.% H₂ at room temperature for 1 h. CO or H₂ desorbed in a temperature range from 300 to 700 K during the TPD.^d The catalysts were pretreated by 4 vol.% H₂ at 373 K for 1 h., H₂ desorbed in a temperature range from 300 to 1100 K during the TPD.^e Not measured.^f TPD spectrum was not given in Fig. 12.

desorbs from Pd/ZnO in a wide range of temperature. For Cs-modified Pd/ZnO, the desorption of H₂ also occurs in a similar wide range of temperature and the total amount of H₂ is also comparable compared with the results for Pd/ZnO. A larger quantity of H₂ desorbing at lower temperatures up to 650 K for the Cs-modified Pd/ZnO catalyst should be an important factor to explain its higher activity for the selective oxidation of CO in H₂-rich gas. The adsorption of H₂ on Pd/SiO₂ is also not strong but the adsorption of CO is strong; this may be responsible for its lower catalytic activity.

The reaction mixture includes both CO and H₂ and competitive adsorption of these gases should occur during the reaction. So, TPD was further conducted after CO (5%) and H₂ (20%) were passed over the catalyst samples at room temperature. The TPD profiles obtained are given in Fig. 12, indicating that these profiles are not so markedly different from those obtained with a single gas species of either CO or H₂. The total amounts of CO and H₂ desorbing during the TPD runs are also given in Table 4. The addition of Cs to Pd/ZnO catalyst affects the desorption of either H₂ or CO; the Cs additive increases the amount of H₂ desorbing at low temperatures up to 500 K, similar to the effect on the single H₂ TPD (Fig. 11). The

amounts of H₂ desorbing from Cs-modified and unmodified Pd/ZnO catalysts are comparable with those for single H₂ TPD as shown in Table 4, and so the Cs additive should give surface sites that can have weaker interactions with H₂. The total amount of CO adsorbed from the mixture of CO and H₂ is smaller for Cs-modified Pd/ZnO catalyst than for unmodified Pd/ZnO one, in contrary to the results for the single CO TPD (Fig. 10). However, from careful inspection of the TPD results of the Cs-Pd/ZnO and Pd/ZnO catalysts of Fig. 12, one may say that the desorption of CO at temperatures about 450 K is hardly observed to occur for the former catalyst; namely, the surface sites that can interact strongly with CO disappear by the addition of Cs to Pd/ZnO. This effect of Cs addition is also seen for the single CO TPD (Fig. 10).

Those results demonstrate that the addition of Cs promoter affects the adsorption/desorption behavior of CO and H₂ on PdZn alloy particles in Pd/ZnO catalysts but not the size of PdZn alloy crystallites. The Cs promoter is effective to provide surface sites on the catalyst that can interact weakly with either H₂ or CO in the mixture of H₂ and CO. The weaker adsorption of H₂ would suppress its undesired consumption with O₂ and produce surface sites useable for CO adsorption followed by oxidation to CO₂. In addition, those sites do not adsorb CO species strongly. As a result, the selective CO oxidation in H₂-rich gas can be enhanced by the Cs-modified Pd/ZnO catalysts. Further works are necessary to elucidate the competitive adsorption of reacting gaseous species in more detail and the reaction mechanisms.

3.7. Comparison with the previous catalysts

Table 5 compares the present catalyst of Cs-modified 1 wt% Pd/ZnO of Cs/Pd = 3 with those in the literature for the selective oxidation of CO in H₂-rich gas under similar conditions. Supported Pt and Ru catalysts show higher CO conversion levels and can reduce the effluent CO concentration to 5 and 0.5 ppm levels, respectively. Potassium-modified Rh catalysts also give better results at a smaller inlet CO concentration of 0.2% in the absence of both CO₂ and H₂O. After considering the differences in the reaction conditions, we may say that our Cs-modified Pd/ZnO catalyst is currently one

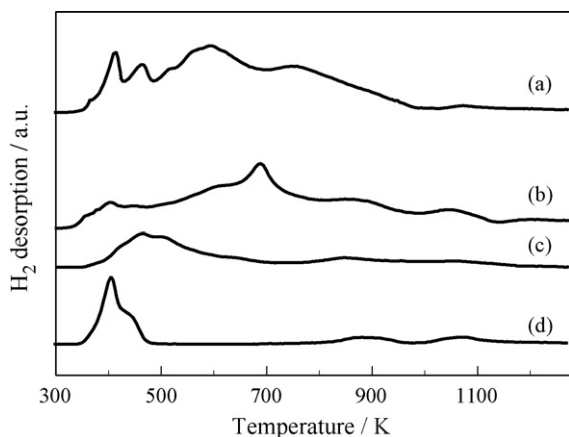


Fig. 11. H₂-TPD profiles for four different catalysts. The catalysts were pretreated by 4 vol.% H₂ at 373 K for 1 h. (a) Cs-modified 1 wt% Pd/ZnO (Cs/Pd = 3), (b) 1 wt% Pd/ZnO, (c) 1 wt% Pd/SiO₂ and (d) 3.7 wt% Cs/ZnO catalysts.

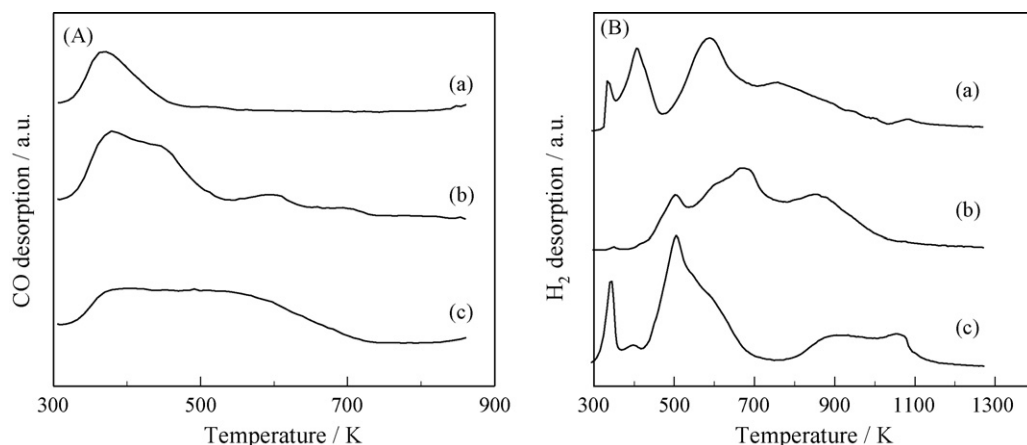


Fig. 12. TPD profiles for four different catalysts. The catalysts were pretreated by a mixture of 5 vol.% CO and 20 vol.% H₂ at room temperature for 1 h. (A) CO desorption and (B) H₂ desorption from (a) Cs-modified 1 wt% Pd/ZnO (Cs/Pd = 3), (b) 1 wt% Pd/ZnO and (c) 1 wt% Pd/SiO₂ catalysts.

Table 5
Comparison of the Cs-modified Pd/ZnO catalyst with the earlier reported ones for the selective oxidation of CO in H₂-rich gaseous mixture under similar conditions

Catalyst	Composition of feed gas (%)					Temperature (K)	SV (h ⁻¹)	W ^a (g)	F ^b (cm ³ min ⁻¹)	CO conversion (%)	CO concentration ^c (ppm)	References
	CO	O ₂	H ₂	CO ₂	H ₂ O							
1 wt% Cs-Pd/ZnO	0.5	2.0	23	7.0	0	433	120000	0.1	117	99.2	40	This work
0.5 wt% Pd/Al ₂ O ₃	0.09	0.23	0.09	0	0	454	20000		10000	70	270	[7]
1 wt% Pd/Al ₂ O ₃	0.11	0.099	1.1	0	0	423		0.2	100	35	715	[25]
1 wt% Pd/C	0.6	0.6	98.8	0	0	438				55	2700	[36]
1 wt% Pd/A-Zeolite	0.5	1.0	37	18	5.0	478	67000	0.15	100	81.4	930	[13]
2 wt% Pt/Al ₂ O ₃	0.5	0.5	65	20	10	423	34000	0.07	40	99.9	5	[8]
1 wt% Ru/Al ₂ O ₃	0.5	0.75	67.75	20	11	393	7500	11.2	1000	99.99	0.5	[10]
2 wt% K-Rh/SiO ₂	0.2	0.2	75	0	0	403		0.025	100	99.5	10	[18]
2 wt% K-Rh/USY	0.2	0.2	75	0	0	403		0.025	100	99.5	10	[18]
100% FeOx/Pt/CeOx	3	1.5	20	0	0	353		1.5	100	80	6000	[27]

^a Weight of catalyst used.

^b Total Flow rate.

^c Concentration of CO in the effluent.

of best catalysts for the selective oxidation of CO in H₂-rich gases.

The catalyst stability against air oxidation under ambient conditions was examined. The optimized Cs-modified Pd/ZnO (Cs/Pd = 3) catalyst was exposed to air at room temperature for 7 days and used without any treatment for the reaction under normal conditions at 433 K. The catalyst was indicated to maintain its previous activity as observed before the air exposure. Namely, this catalyst has a durable activity against air oxidation.

4. Conclusions

Various supported Pd catalysts on ZnO, Ga₂O₃, SiO₂, CeO₂, In₂O₃, and Al₂O₃ were screened for the selective oxidation of CO in H₂-rich gas. The Pd/ZnO catalyst in which Pd is alloyed with Zn is most active compared with the other catalysts that contain metallic Pd and/or other Pd alloys (in Pd/Ga₂O₃). The reduction temperature affects the activity of Pd/ZnO catalyst and the sample reduced at 773 K is more active than that at 473 K because 473 K is not sufficient for Pd species to change to the PdZn alloy. The activity level of Pd/ZnO catalyst reduced at 773 K is not high for practical application but it can be

significantly enhanced by the addition of alkali compounds, in particular Cs. The Cs additive enhances the CO oxidation but suppresses the H₂ oxidation. The optimized Cs-modified Pd/ZnO catalyst (Cs/Pd = 3) is able to reduce the CO concentration of a mixture of CO/H₂/O₂/CO₂ (1.6/23/2.0/7.0 in N₂) to a 40 ppm level at 433 K, while controlling the H₂ conversion level to <10%. In addition, the catalyst has a durable activity against air oxidation. The adsorption/desorption behavior of CO and H₂ on PdZn alloy particles is an important factor responsible for the activity enhancement observed but the size of PdZn alloy crystallites is less important. TPD measurements indicate that the Cs promoter should provide surface sites that can interact weakly with either H₂ or CO in the mixture of H₂ and CO. This would suppress the undesired consumption of H₂ with O₂ and produce surface sites useable for CO adsorption followed by oxidation to CO₂. Thus, the selective CO oxidation in H₂-rich gas can be enhanced by the Cs-modified Pd/ZnO catalysts.

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